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TORSIONAL RELAXATION IN POLYCRYSTALLINE CADMIUM AS A FUNCTION OF SURFACE PHENOMENA

BURTON I. EDELSON

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BURTON I. EDELSON

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TORSIONAL RELAXATION IN POLYCRYSTALLINE CADMIUM AS A FUNCTION OF SURFACE PHENOMENA

A Thesis
Submitted to
the Faculty of the Department of Metallurgy
Graduate School, Yale University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Burton I. Edelson, B. S.
U. S. Naval Academy, 1947
October 1953

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Abstract

An investigation of the tortional after-effects in polycrystalline cadmium wires which had undergone torsional plastic deformation was made. The influence of surface phenomena on relaxation rates was studied. Relaxation rates of clean wires were not influenced by the surrounding media; air, distilled water and dilute sulfuric acid. Relaxation rates of wires which had an oxide surface film were greater than those of the clean wires, and application of acid to oxidized wires caused reversals in the strain versus log time relaxation curves. Cold working caused the initial strain rate to increase; annealing prior to oxidation caused it to decrease. Increasing film thickness did not affect relaxation rate but lengthened the time during which reversal occurred. Delay in applying acid to oxidized wires increased the amount of reversal and the time for it to occur. Oxidizing the wire after twisting caused the initial strain rate to be smaller, but when acid was applied the rate became greater. The results are explained by assuming the oxide films to act as elastic, coherent jackets which modify the normal relaxation rates of the bare wires.

TORSIONAL RELAXATION IN POLYCRYSTALLINE CADMIUM AS A FUNCTION OF SURFACE PHENOMENA

Introduction

It has been demonstrated in many experiments conducted in recent years that various physical properties of metals may be drastically altered by varying the surface conditions. Not only have the explanations of these changes been questioned and debated, but in some cases attempts to reproduce the effects themselves have been unsuccessful. The properties of metals that have been investigated in this regard are creep rate, critical resolved shear stress and, more recently, torsional after-effects. Surface condtions that have been correlated with the above include (1) presence or absence of oxide, hydroxide, sulfide and electroplated metal films, (2) electric potential, and (3) properties of the environmental medium such as activity and viscosity. Quantitative work has been attempted in some cases, but the nature of the experiments does not lend itself easily to exact reproduction by different investigators. As will be seen by a review of the literature published on these effects, there are nearly as many theories accounting for them as there are investigators.

In 1934 Roscoe[1] discovered that the presence of an oxide film on cadmium single crystals increased the critical shear stress considerably. Removing the oxide film with acid restored the lower critical shear stress of an unoxidized crystal.

Rehbinder and coworkers[2] studied the creep rate of monocrystalline tin wires, as effected by organic acids dissolved in hydrocarbon solvents. He found that the creep rate was increased by an order of magnitude of two or three times after a significant time delay following the application of acid. He postulated that the organic acids were absorbed in surface cracks. Here they widened the cracks and introduced stress concentrations facilitating the glide process. This explanation ignores the presence and attack on an oxide layer which might be present. He also reported a great change in the electrical resistivity after a large elongation. The increase in resistivity disappeared after the release of tensile force. This, he claimed, substantiated his theory of the formation of cracks.

Some of the effects which Rehbinder reported have since been re-evaluated. Harper and Cottrell[3] tested zinc oxide single crystals under similar conditions and found similar creep behaviour. They found the time delay which Rehbinder reported to be proportional to the viscosity of the medium. Further, they examined quantitatively various surface preparations, namely, etching, electro-polishing and steaming, and reported that the heavier the oxide film the greater the critical resolved shear stress (for constant extension). Significantly, they found that the oxide film had a dynamical rather than a static effect, determined by the amount and rate of flow rather than by the initial stress required to start flow. Finally they

attempted a correlation of previous findings and postulated that the primary effect is the hardening produced by the film and that the organic solutions used by Rehbinder merely modified the action of the film by penetrating cracks in the film and weakening the surface adherence.

The strengthening effect of films was found by Andrade and Randall[4] in zinc and cadmium single crystals immersed in salt solutions. They were unable to find any effect in polycrystals. Kemsley[5] was unsuccessful in reproducing the increase in resistivity noted by Rehbinder.

Masing[6] correlated creep rate of various metals in salt solutions with the application of an electric potential. He found that increasing the absolute magnitude of the electric potential (either positive or negative) increased the elongation rate under constant stress. The same effect occurred with the noble metals, gold and platinum, which form no oxide layer. His co-workers were able to reproduce the effect of Rehbinder on the increase of the creep rate in active hydrocarbon solutions with zinc and even gold. They were entirely unsuccessful, like Kemsley, in reproducing the resistivity effect.

Phillips and Thompson[7] tested the effect of various salt solutions on creep of cadmium single crystals. The film was identified as $Cd(OH)_2$ and its thickness was correllated with reduction of creep rate. Again no effect was noted for cadmium polycrystals.

Coffin and Weiman[8] have recently published quantitative studies on the effect of surface composition on the creep rate of monocrystalline zinc. They examined the creep behaviour in air and in acid of crystals with clean surfaces and with sulfide and oxide films. The increase of creep rate noted upon acid attack is attributed to two causes: (1) that the surface film carries part of the load and its dissolution weakens the crystal considerably, and (2) the thermal transient caused by the acid reaction contributes to the change in creep rate. The former is substantiated by the recognized fact that extremely thin materials approach their theoretical strength; the latter, by assuming localized heating with slow dissipation and noting that a slight increase in creep rate was found in "clean" crystals. The increase of creep rate was large only for low extensions, the cracks in the oxide film allowing the metal to creep at its normal rate. The very small increase in creep rate at high extensions they attributed to heat effect.

Barrett[9, 10] has discovered and developed rather startling effect which was previously predicted from theoretical considerations only -- always a very heartening experience for theoretical scientists. It was suggested by A. H. Cottrell in a private communication in 1951 that, according to dislocation theory, it would be possible to alter the normal after-effect of a metal by removing a coherent surface film.

If a metallic wire is twisted beyond its elastic limit and the applied stress then released there occurs an instantaneous elastic recovery followed by a time-dependent relaxation. This relaxation, called the normal after-effect, is such that the wire recovers, approximately, an equal number of angular units in equal increments of the logarithm of time.[11] For the most part then, if recovery in degrees is plotted against log time a straight line will result. Actually, the curve is flat at time zero and at infinite time -- but the central portion of the curve, the straight line part, is the easiest to use and most conveniently obtained if the first few seconds are ignored and the wire is observed for a reasonable period of time, say one hour.

Cottrell originally postulated, and Barrett developed the theory, that a sudden release of dislocations piled up beneath a coherent surface layer would alter this normal after-effect. The twisting of the wire, according to this theory, causes dislocations to be piled up just below the surface of a coherent film. Release of the stress allows these dislocations to migrate back toward the center of the wire. This untwisting is the normal after-effect. If, during the untwisting, the surface layer could be quickly removed, by etching for example, those dislocations still piled up at the surface would be released to escape from the metal. This is an opposite motion to the existing motion of dislocations, and, therefore, should evidence itself by an opposite movement

of the wire, i.e., a tendency to twist. Barrett[9, 10] has observed this phenomenon in single crystals of zinc and in polycrystals of iron, zinc and cadmium. In some cases, those in which the number of dislocations escaping from the surface more than compensated for the number of migrating back to the interior of the wire, the wire actually reversed upon removal of the surface layer (abnormal after-effect). In those cases where the number of dislocations escaping was not great enough to overbalance the number migrating to the center, the untwisting was merely slowed and the resultant plot showed a decrease of slope.

In his first paper Barrett merely established the existence of the effect in zinc and iron. No attempt was made at precision timing and thus only poor reproducibility was obtained. The second paper showed a similar abnormal after-effect in polycrystalline cadmium. The effect was found when an oxide film formed in air was attacked by a wwak sulfuric acid solution; a substantially greater abnormal after-effect was found when a film formed by anodization in sodium hydroxide was attacked by the same acid. No change in slope or abnormal effect was found in a control run with a "clean" wire, the product of one of the previous runs. Based on the above, certain conclusions were drawn: (1) that the control test indicated the abnormal effect did not originate from a thermal transient or acid attack on the metal itself; (2) that the sensitivity of the method was great enough to detect very thin films (those formed in air at room temperature in

less than an hour); (3) that moderate plastic deformation did not interrupt the coherency of the film in causing this effect, and (4) that prior cold work increased the magnitude of the normal after-effect and a delay in etching time decreased the magnitude of the reversal.

An alternate theory for explaining the abnormal after-effect was evaluated. Fisher[12] has shown that less stress is required to activate a Frank-Read dislocation generator at the surface than in the interior of a crystal. The presence of a film would tend to keep the former inactive. Barrett contends, however, that upon the removal of the surface film, the generators then springing into action would have equal tendencies to twist and untwist and consequently contribute as much to the normal as to the abnormal after-effect.

The apparatus used in the above experiments was very simple. The wires were hand twisted so that the exact number of degrees of twisting was unknown. Also the possibility of introducing a bending, tensile or compressive stress existed. Precision timing again was not attempted so adequate reproducibility was not obtained. Buoyancy effects on the mirror were not evaluated and effective length of the wire could not be standardized in such an apparatus. More quantitative work is now in progress by Barrett on high purity aluminum.

In addition to the explanations considered by Barrett -- namely (1) the existence of a barrier to escaping dislocations,

(2) the inhibition of dislocation generators and (3) the possibility of thermal transients -- there exists the possibility, analogous to the strength of oxide coatings postulated by Coffin and Weiman[8], that the surface films actually are coherent elastic films. That is to say, the surface film exhibits a greater degree of elasticity than the metal itself. Twisting of the film and the wire causes internal stress in the surface film which tends to relieve itself elastically, this in turn causing the wire to recover at a greater rate than it would by itself. The removal of this film allows the wire to seek its own recovery rate, even reversing temporarily to the position it would have assumed were the film not originally present. Such a simple theory could account for the phenomenon observed and must not be ruled out until quantitative measurements have excluded its possibility as an explanation.

In this research an attempt has been made to obtain quantitative data from which more precise conclusions might be drawn. The goal to be approached is a measure of reproducibility adequate to show the exact effect of varying the different parameters of the run. By that means it should be possible to exclude one or more of the aforementioned theories and arrive at a perfectly consistent and unique explanation.

Specifically, precision timing is essential to obtain data that is directly comparable, run for run. The results which

are important are the initial slope and the amount and duration of abnormal after-effect. If reproducibility of these measurements could be obtained the following paramenters might be varied individually:

(1) Previous history of the wire (cold-working and annealing.)

(2) Holding time after twist and prior to release of wire.

(3) Time of applying the etchant.

(4) Thickness of the film.

(5) Order of applying film and twisting.

With a consistent set of data from the above outlined experiments it should be possible to arrive at the most plausible theoretical explanation.

Investigations of this kind must be highly specific, therefore, a particular metal and a particular film type were chosen which would yield the most significant and easily evaluated data.

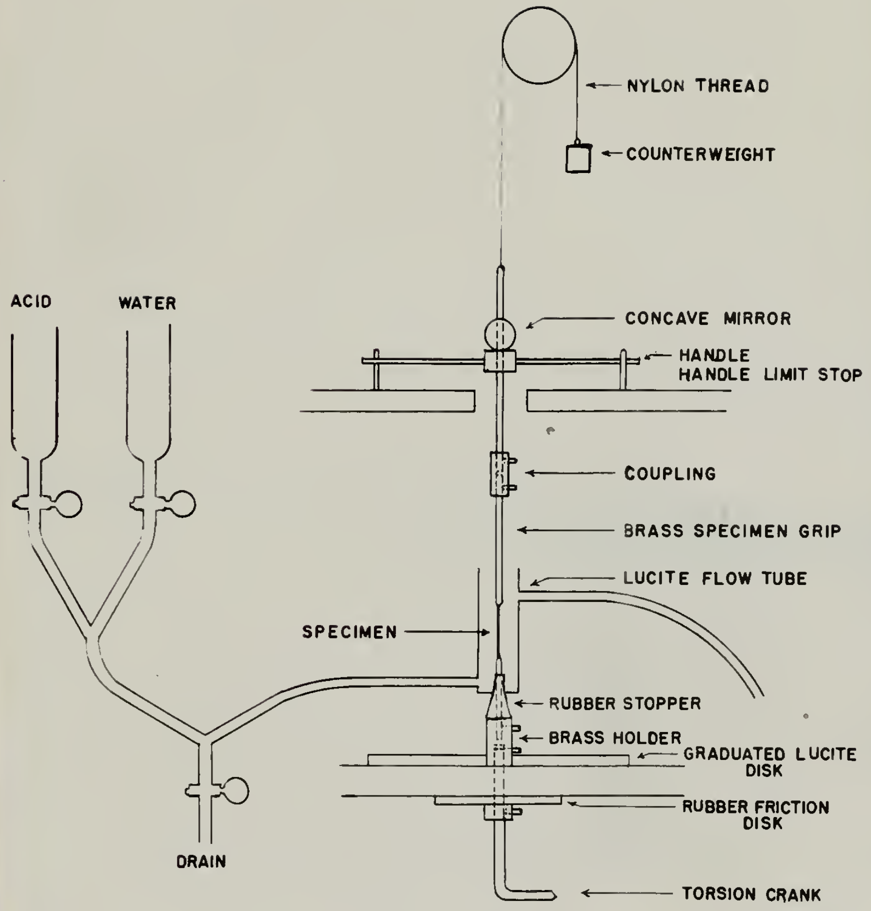
Method

Apparatus. For preliminary work the apparatus developed by Barrett[10] was used. (See Figure 1.) This was a very simple machine to construct and served very well to select a metal and a type of film to produce the best effect. The apparatus was used to obtain the first set of data which is described later.

Fig. 1. Photograph of preliminary apparatus. Specimen is cemented to brass crank and to glass fiber which supports mirror.

For more quantitative work it was found necessary to design apparatus which would afford greater reproducibility. It was necessary to obtain precision timing, to eliminate accidentally introduced bending, tensile and compressive stresses, to control the exact amount of twist, time of holding after twist, possible buoyancy, wetting and thermal transient effects, and, as later developed, to allow the application of a surface film subsequent to twisting.

The apparatus shown in Figures 2, 3, and 4 was developed to meet the above requirements. The wire specimens, each 5.6cm long and 1.11mm in diameter, were cemented in 1/8" brass grips using "Cenco-Sealstix" wax, a DeKhotinsky type cement, with a softening point of about 140° C. Length of specimen between grips measured 4.0cm. (See Figure 5.) Extreme care was used to avoid working or annealing the wires as they were fastened into the grips. No evidence was found of plasticity in the cement. The bottom grip was secured into a brass holder by means of an Allen set screw. The holder was rigidly fastened to a graduated lucite disk and to the crank which extended below the base of the apparatus cage for twisting the wire. Amount of twist was ready by matching the graduated disk with a line on the base of the cage. The top grip was rigidly coupled to another 1/8" brass rod which extended through the top of the cage, and to which was secured a handle and concave mirror. This rod was maintained vertically by a nylon thread and a counterweight. A lucite flow tube



SCHEMATIC DRAWING OF APPARATUS

Figure 2. Schematic Drawing of Final Apparatus.

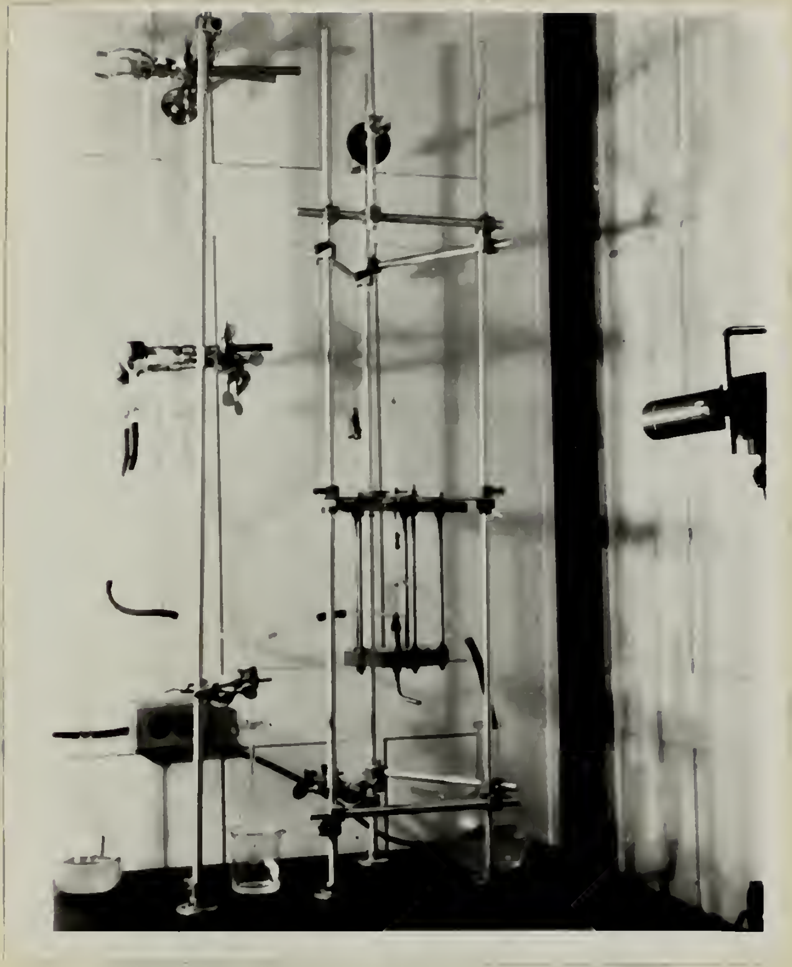


Figure 3. Photograph of Final Apparatus.

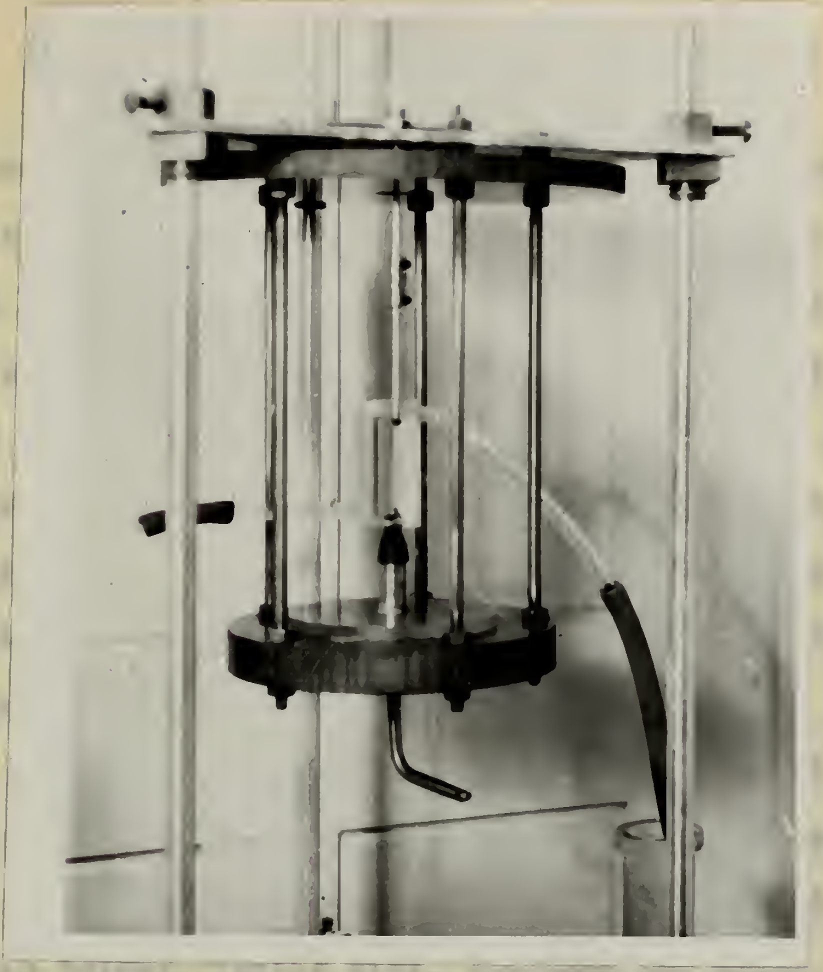


Figure 4. Closeup of cage of final apparatus. Specimen may be seen in liquid in flow tube.

Figure 5. Photograph of specimen and specimen grips.

surrounded the specimen permitting a liquid medium to surround the wire. Leakage at the bottom of the flow tube was prevented by a rubber stopper, through which was inserted the lower specimen grip. Two burettes were connected to the inlet of the flow tube, and they permitted changing of the medium from water to acid, as desired. A drain valve and overflow tube were also provided. In this way liquid level remained constant and the specimen was always wet. Thus there was no buoyancy or wetting effect.

The apparatus permitted the wire to be twisted, held, released and its relaxation observed with a minimum of handling in the following manner. When the crank was turned, the grip holder, lucite disk, specimen and grips, and the handle and mirror turned with it; whereas the flow tube and rubber stopper remained stationary. If the crank were turned far enough, the handle encountered two handle stop limits, fixed to the top of the cage, which prevented its further turning. This fixed the top of the specimen, upper specimen grip and mirror in the "zero position". Further turning of the crank would twist the specimen. When the specimen was twisted the required amount and held for the prescribed time the crank was backed up until the handle was well free of the limit stops; zero time was marked; and the specimen was allowed to relax. Untwisting of the wire was transmitted to the mirror through the upper grip, since the bottom grip, holder and crank were maintained fixed by a rubber friction disk.

A lamp and scale device together with a timer were used to record the movement of the mirror. The scale was set 113" from the mirror so that centimeters on the scale were directly convertible into tenths of degrees for plotting.

All runs were made at room temperature (23° to 25° C). All wires were twisted 180° in approximately 4 seconds. The etchant used in every case was 2% H_2SO_4. The control medium was distilled water, both media at room temperature. Unless specifically stated otherwise the following parameters were kept constant. The time from commencement of twist to release of load was 30 seconds. The wire was twisted, held and allowed to relax surrounded by distilled water. The etchant was applied at 400 seconds.

<u>Preparation of Specimens</u>. Preliminary work on this research and that of Barrett[10] indicated that the abnormal after-effect was especially marked in anodized cadmium. For that reason polycrystalline cadmium was investigated exclusively. The metal was obtained in cast ingots from the New Jersey Zinc Company. Spectroscopic analysis showed that it contained:

> commercially pure cadmium, all
> impurities less than 0.1%.

Wires were prepared as indicated below.

<u>A-Cadmium</u>. This wire was obtained by casting a bar in 1/4"

graphite mold and rolling with frequent annealing between operations to 5mm diameter. Then the wire was cold drawn to 1.11mm without further annealing (approximately 95% reduction in area). The wire was then successively washed in kerosene, carbon tetrachloride, sulfuric acid, distilled water and methanol. Finally it was cut into 5.6cm lengths.

B-Cadmium. Same as A, except annealed at 1.36mm (approximately 35% red. in area).

C-Cadmium. Same as A, except annealed at 1.22mm (approximately 17% red. in area).

D-Cadmium. Cast in 13mm ID pyrex tube and rolled with frequent annealing to 3mm, then drawn with frequent flame annealing between draws to 1.11mm. Flame annealed at 1.11mm and washed as A.

E-Cadmium. Cast in 1/4" graphite mold and cold rolled to 3.5mm and drawn with frequent flame annealing to 1.80mm. Then cold drawn without further annealing to 1.11mm. Washed as in A.

Anodizing Procedure. A very simple arrangement was used to form anodic films on the cadmium specimens. The cell consisted of the specimen as anode, a platinum cathode, and 1N sodium hydroxide as electrolyte. It was found that 2.5v gave a very satisfactory anodic film. The current-voltage curve for this cell however breaks at this point so current had to be closely regulated also. This voltage produced a current of .023 amp/cm^2. The film formed was cadmium hydroxide,[13] which

is insoluble in NaOH and water but dissolves readily in 2% H_2SO_4. The time of anodization, unless otherwise stated, was 20 minutes.

Data and Results

Preliminary Tests. Preliminary work established the proper preparation of specimens, anodizing procedure and technique involved in obtaining a large abnormal after-effect. It was then decided to use the apparatus of Barrett[10] to obtain the effect of previous history of the specimen on the abnormal after-effect. Specimens of D-Cadmium were annealed for one hour at various temperatures and then anodized as previously described. The wires were then tested in the apparatus. First the wire was twisted 180° by holding the bottom of the specimen in one hand and twisting the crank with the other. Then a beaker of water was brought up to cover the wire. At 600 seconds the water was replaced by the sulfuric acid. The acid dissolved the anodic film readily. This could be easily seen since the dark brown surface quickly changed to a shiny metallic surface as the film was etched off. A plot of recovery in degrees versus logarithm of time after release of load was obtained for each specimen and the results are shown in Figure 6. The abnormal after-effect (reversal) was found in each specimen except that which was annealed at 290°. Here it may have been too small to notice,

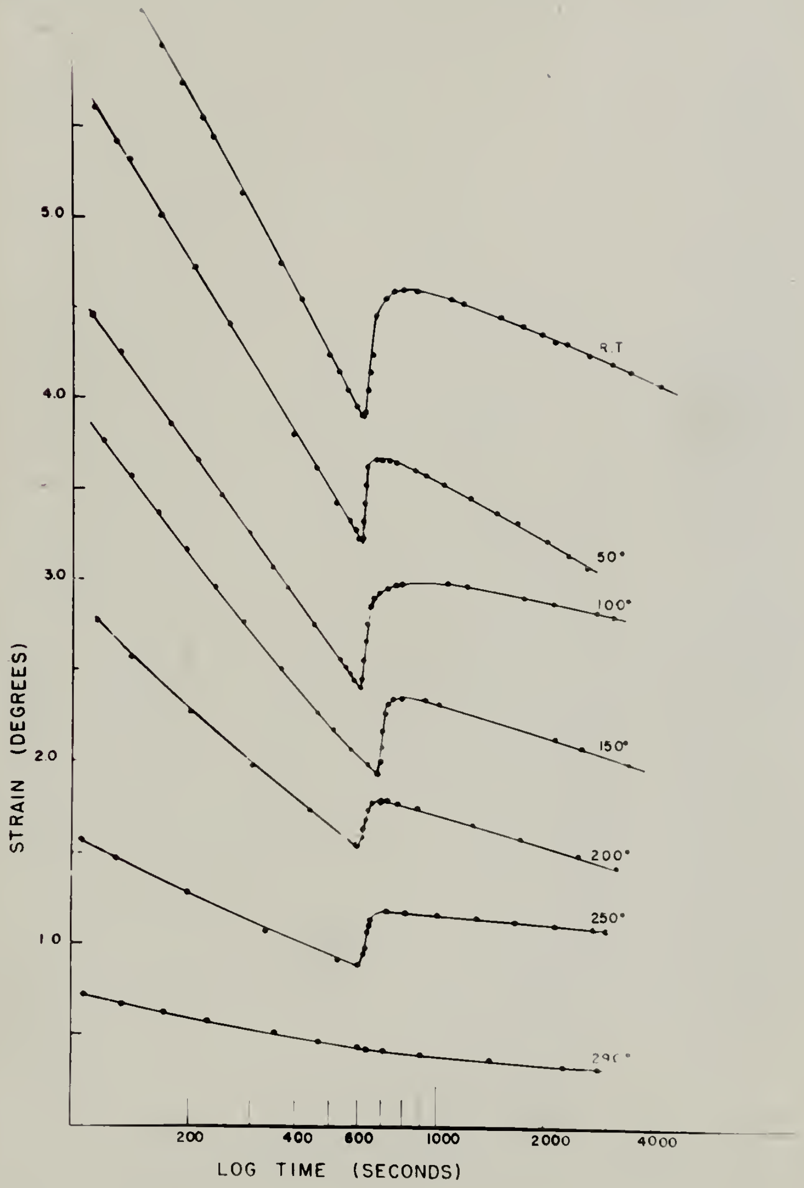


Figure 6. Effect of annealing for one hour at various temperatures on torsional after-effect curves of polycrystalline cadmium (D-Cadmium).

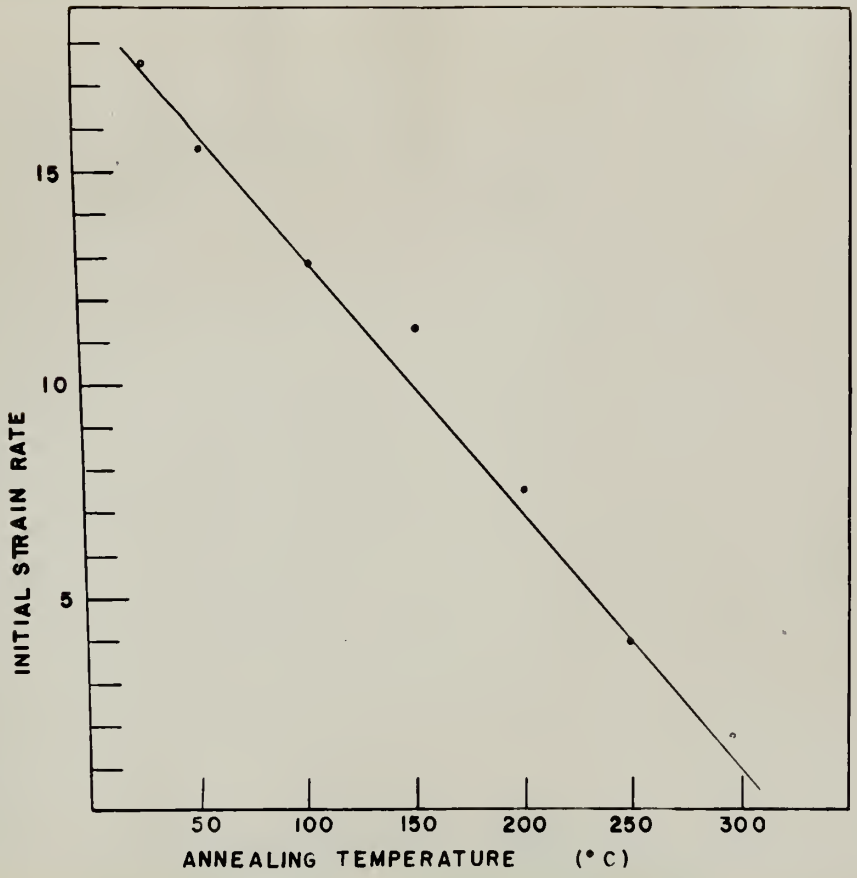


Figure 7. Effect of annealing at various temperatures on initial strain rate (D-Cadmium).

especially since the initial slope was very slight. A summary of the results of this series is given in Table I.

Table I

Run No.	Temperature of Anneal (°C)	S_1	R
66	Room Temp.	17.5	7.1
73	50	15.5	4.4
68	100	12.8	5.7
69	150	11.3	4.6
70	200	7.4	2.6
71	250	3.9	3.1
72	290	1.7	-

In this table S_1 represents the initial slope of the plot prior to etching expreseed in tenths of degrees per log 3 seconds. (Specifically, the number of tenths of a degree of strain recovered between 200 and 600 seconds). R represents the magnitude of the reversal in tenths of a degree.

The initial slope decreased with increasing annealing temperature (See Figure 7). No direct conclusion could be drawn concerning the amount of reversal as a function of annealing temperature. Reproducibility in these runs was poor. The above runs were made many times and those selected were representative of their group.

Effect of Cold Work. The apparatus shown in Figures 2-5 and previously described was used in all subsequent investigations. This apparatus could be more closely controlled and the results were more consistent and less subject to operator manipulations. A-, B- and C-Cadmium were identically prepared except for the amount of cold work. After standard anodizing treatment these wires were tested to determine the effect of cold working on the normal and abnormal after-effects. Figure 8 shows the plots obtained from samples of each cold-worked wire. Results are tabulated in Table II.

TABLE II

Run No.	Cadmium	Percent Reduction in area	S_1	R
88	A	95	12.8	6.4
91	B	35	9.7	6.0
92	C	17	7.9	4.5

In the above table, and all succeeding ones, S_1 is the strain rate or initial slope prior to etching expressed in tenths of a degree per log 2 seconds. (The amount of strain recovered between 200 and 400 seconds.) R is the reversal in tenths of a degree.

As might be supposed, increasing amounts of cold work tend to increase the normal strain rate when the anodic coating is the same. The number of samples here is too small to analyze the effect on R.

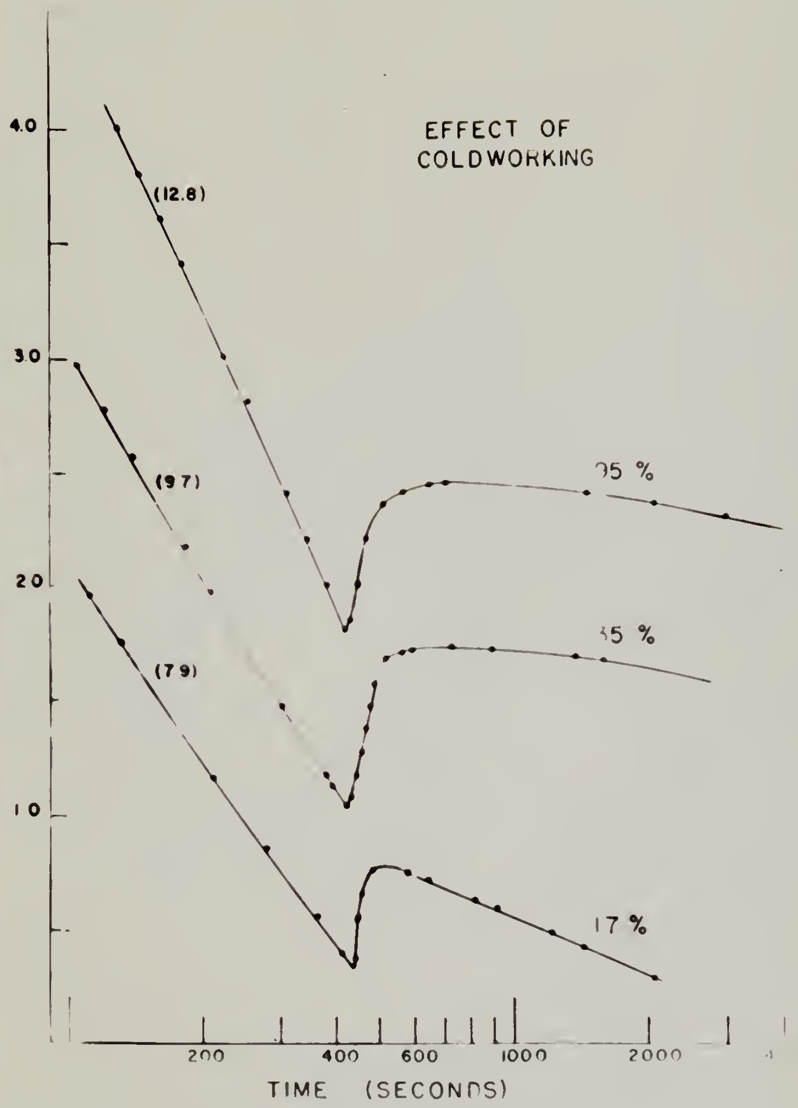


Figure 8. Effect of cold work on after-effect curves. Numbers in parenthesis indicate initial slopes (strain rate). Percentages indicate amount of reduction in area after last anneal.

Effect of Annealing Temperature. Using the highly cold worked A-Cadmium, a more comprehensive series of tests was made. The first was an attempt to repeat the series previously run in the simpler apparatus to get more precise results. Accordingly, specimens of this wire were annealed in air at various temperatures for one hour, then anodized in the standard manner for 20 minutes. It is considered that any oxidation of the surface occurring during the high temperature anneal would be destroyed or converted to the hydroxide in the anodizing process.[13] Finally, the specimens were mounted in the grips and tested in the standard manner in the apparatus. The plots of strain versus log time after release of load are given in Figure 9 . The plots are summarized in Table III.

Table III

Run No.	Anneal Temp. (°C)	S_1	R
101	R.T.	13.2	5.4
96	150	9.2	3.2
97	250	4.0	3.3
105	290	1.8	2.4

A reversal was found in every case in this series. These runs, made in the improved apparatus, were more reproducible

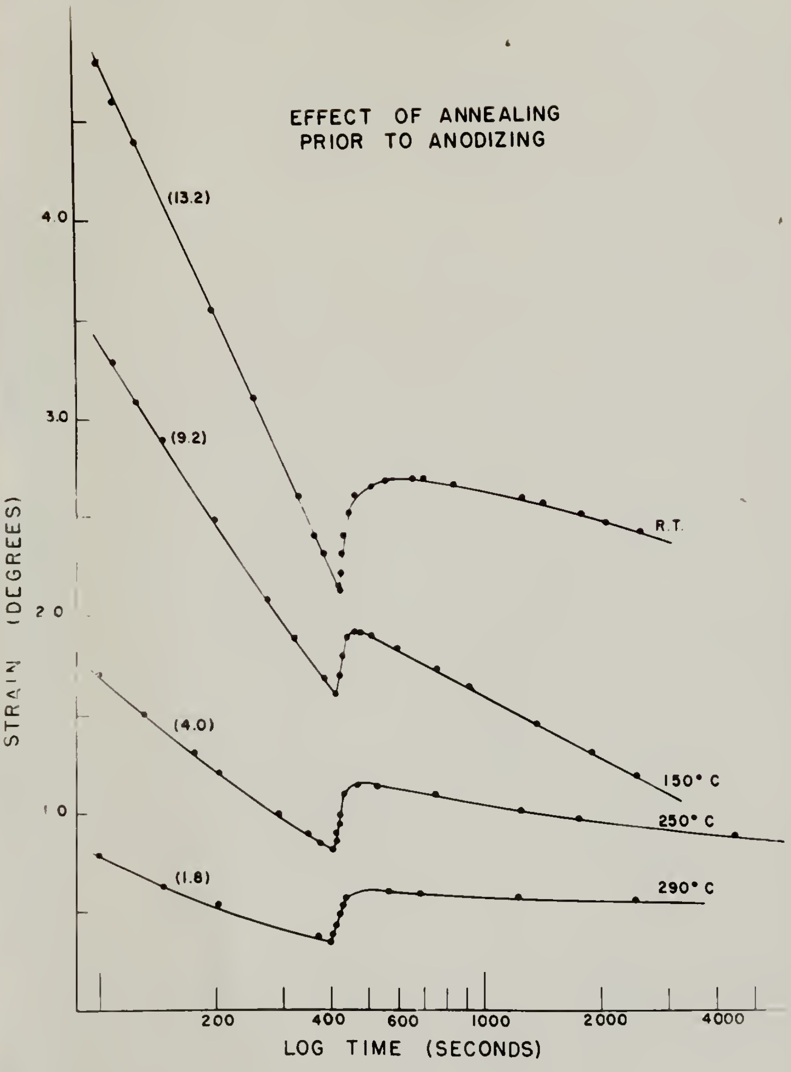


Figure 9. Effect of annealing for one hour at various temperatures (A-Cadmium).

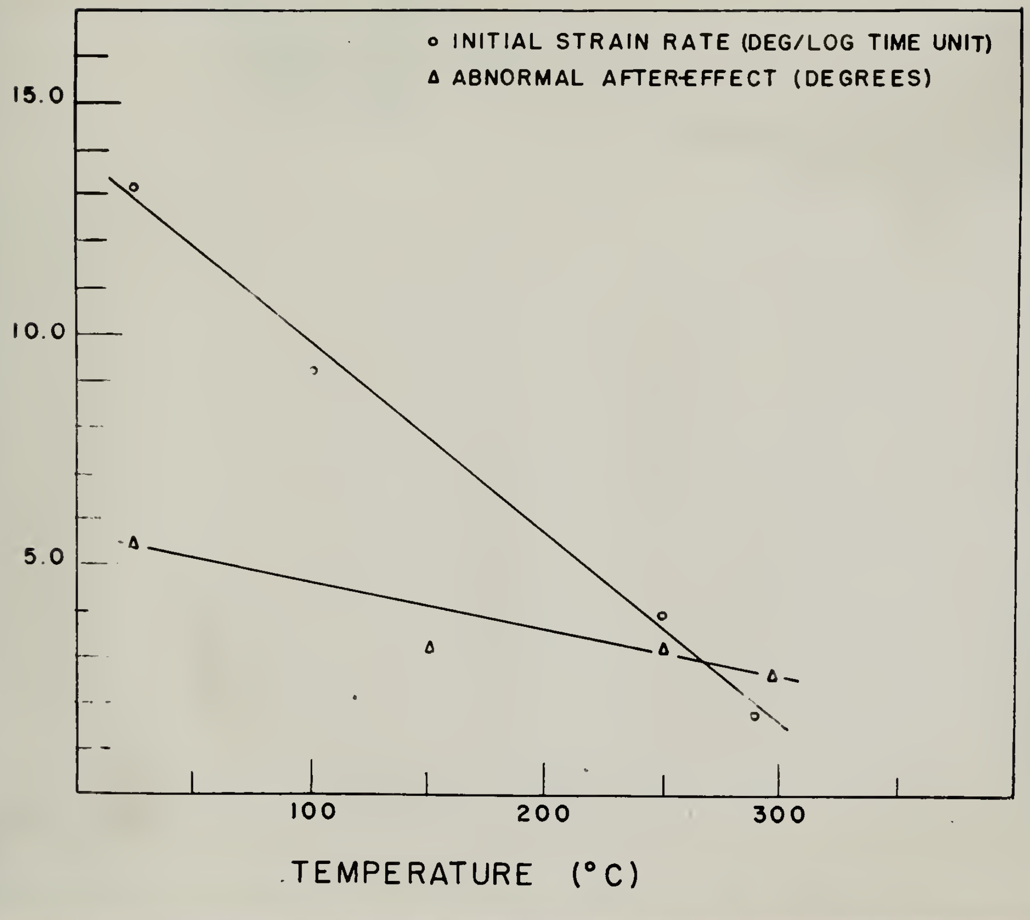


Figure 10. Effect of annealing at various temperatures for an hour prior to anodization on initial strain rate and amount of reversal (A-Cadmium).

and are considered more precise than those shown in Figure 5. Here, the initial strain rate again became less with increasing annealing temperature. The amount of reversal, R, also decreased with increasing annealing temperature. These two functions are plotted in Figure 10.

Thus far the only variable observed has been the previous history of the metal, namely annealing temperature and amount of cold work. It would seem only natural that the more cold worked a specimen is and the smaller its grain size, the higher would be its strength properties. Twisting of a specimen with less internal stress should produce a greater amount of plastic deformation. The cold worked wire with its greater initial internal stress will experience a lesser amount of plastic or permanent deformation and should be expected to recover more and at a higher rate. This is precisely. what has been shown. Any effect of the anodic coating would be additive to that of the metal and since the anodic coating has not been varied up to this point, no conclusion can be drawn as to its effect on the initial strain rate and the reversal.

Effect of Anodizing. An investigation was made to determine the effect of an anodic coat on the initial strain rate. β-Cadmium was used. The tests were conducted in quadruplicate: four specimens were anodized in the usual manner, and four were etched in 2% $H_2 SO_4$ for five minutes prior to the run. All runs were similar and made in the

standard manner. These runs served as control runs and indicated the degree of reproducibility obtained in addition to showing the marked difference in initial strain rate between the previously anodized and the non-anodized specimens. The resultant plots are shown in Figure 11, and the data tabulated in Table IV.

Table IV

Run No.	Anodized	S_1	S_2	R	(Fig. 11)
88	yes	12.8	2.1	6.4	-A-
89	yes	13.7	1.3	5.5	-B-
101	yes	13.2	1.5	5.4	-C-
102	yes	11.3	1.0	4.9	-D-
114	no	2.8	-	-	-E-
114'	no	2.6	-	-	-F-
114A	no	3.1	-	-	-G-
114B	no	2.6	-	-	-H-

S_2 represents the strain rate after etching (the number of tenths of a degree recovered between 1000 and 2000 seconds). Referring to Fig. 11, curve -F- was obtained using the same specimen as curve -E-, the others were all different specimens. Water replaced acid at point marked "W" on curve -B-. No effect was noticed. Acid replaced the control media, water, at point marked "A" on curves -E- and -G-. Again no effect was noticed. At no time was acid attack of the metal

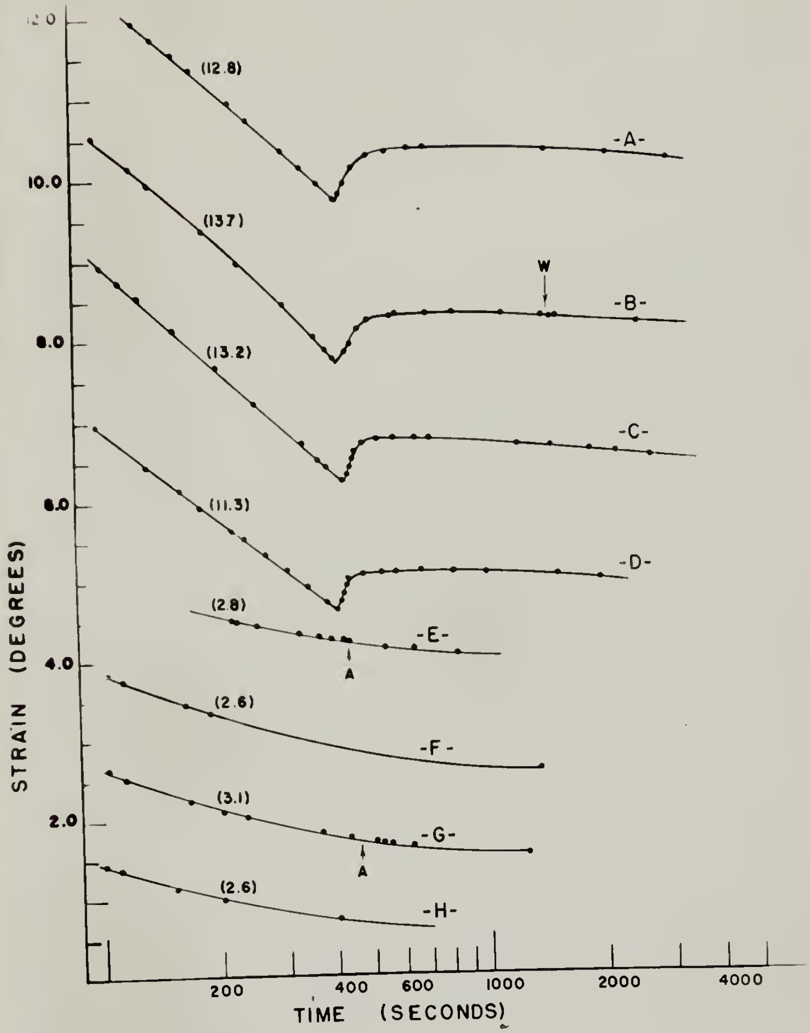


Figure 11. Comparison of after-effect curves of anodized and non-anodized specimens. Curves are in quadruplicate: -A- through -D- were anodized; -E- through -F- were not anodized. "W" indicates water added. "A" indicates acid added. (A-Cadmium)

indicated, either by bubbling or by change in diameter of the specimen after the run.

Theeffect of the anodic coating was to increase the initial strain rate considerably, by a factor of about 4. The reversal of abnormal after-effect did not occur with the "clean" wires. These are two points on which later conclusions are largely based.

Effect of Holding Time: Normal After-Effect. Since the "clean" wire did not behave like the anodized wire, it was found necessary to establish the character of the normal after-effect occurring in a wire with the surface film not present. E-Cadmium was used for all succeeding runs.

A group of non-anodized specimens were twisted in distilled water, held for various lengths of time and released. The plot of strain versus log of elapsed time after release of load indicated that the initial strain rate varied with the time held before release. Figure 12 shows this plot. In all cases the resultant plot is not exactly a straight line, but rather an "S" shaped curve which would extrapolate to zero slope at zero time and at infinite time. The central portion may appear linear for a relatively long period of time. However to be strictly comparable, the slopes must be computed during the same time interval, in this case between 200 and 400 seconds. Examination of the slopes for various holding times in Figure 12 shows that, in the segments plotted, the first three slopes are decreasing in value with increasing time, the

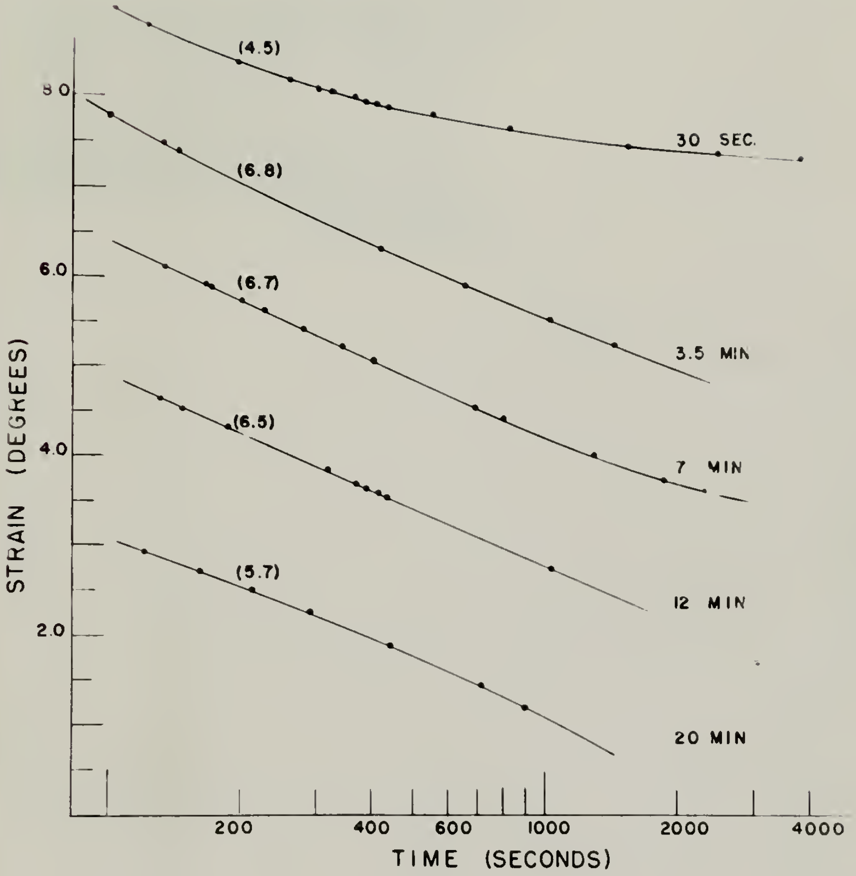


Figure 12. Effect of holding time on after-effect curves of non-anodized wires. Holding time was computed from commencement of twist to release of load. (E-Cadmium)

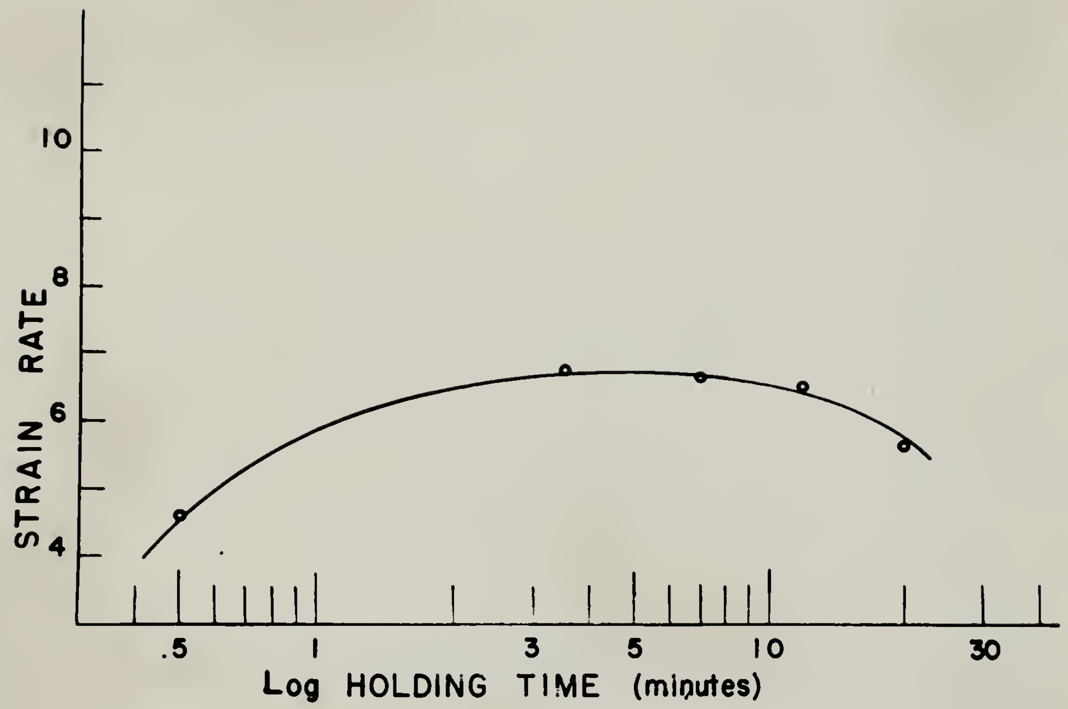


Figure 13. Effect of holding time on strain rate of non-anodized wires. (E-Cadmium)

12-minute curve is almost linear, and the 20-minute curve increases in value. It appears then, that these curves have typical anelastic characteristics; increasing the holding time has the effect of moving the inflection point to later time. The slopes during identical time intervals first increase and then decrease with increasing holding time as shown in Figure 13 and Table V.

Table V

Run No.	Time from Commencement of twist to Release	S_1
115	30 seconds	4.5
115A	" "	4.6
131	3½ minutes	6.8
123	7 minutes	6.7
136	12 minutes	6.5
120	20 minutes	5.7

Effect of Thickness of Oxide Film. Since the pressence of the anodic film had a great effect on slopes, a series of runs was made to determine the effect of thickness of the anodic film. Successive specimens of E-Cadmium were anodized for various lengths of time, all at 2.5v. These specimens were tested in the apparatus and given the standard treatment. The usual plot was made and is shown in Figure 14. Approximate anodization times could be noted visually: the 1-minute film was a very hard blackish-brown; films produced by longer

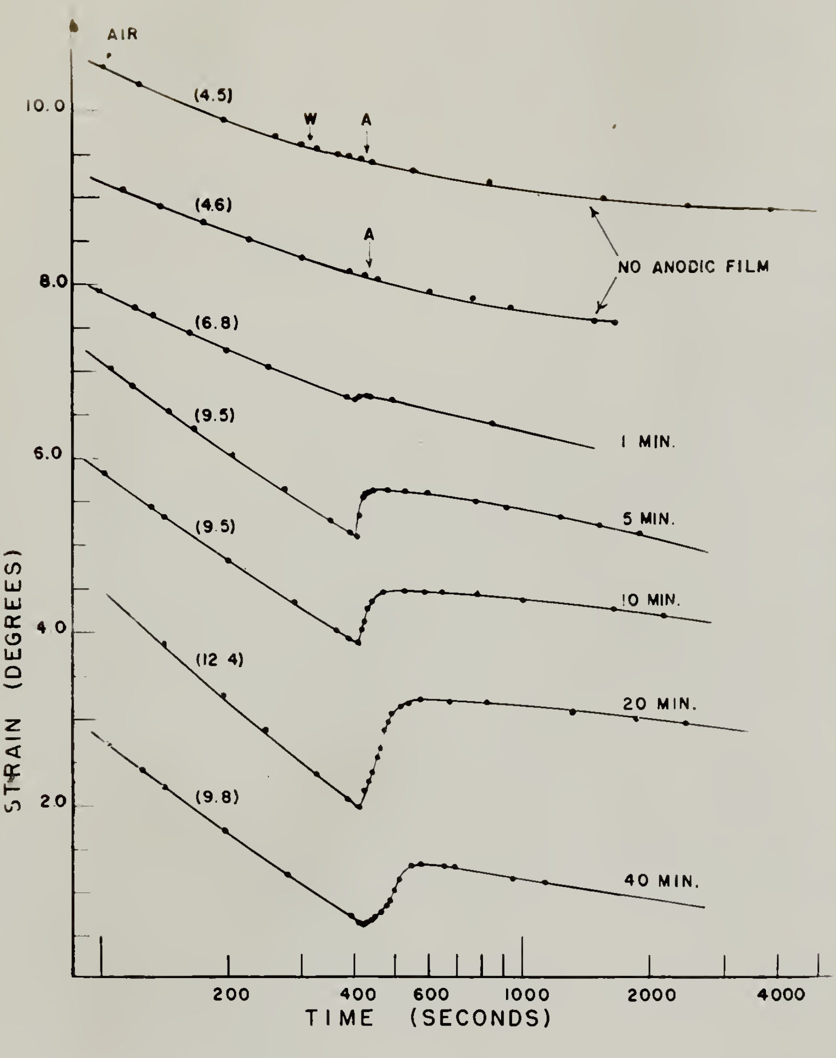


Figure 14. Effect of anodizing time at 2.5v on after-effect curves. (E-Cadmium)

anodizing time were successively lighter; and the 40-minute coat was a very light grey, appearing slightly spongy. The non-anodized specimens, which of course were a shiny metallic color, showed no reversal upon application of acid (applied at "A" in Figure 14). The 1-minute specimen showed only a very slight reversal. All others indicate an appreciable reversal of the same order of magnitude, although the longer the anodization time the longer was the time during which reversal took place. The two non-anodized runs were identical, except that as an additional control the first run (#115) was twisted and released in air and distilled water first added at 300 seconds. This treatment had no evident effect on the resultant plot. The data for these runs is tabulated in Table VI.

Table VI

Run No.	Anodization time	S_1	R	t
115	0	4.5	-	-
115A	0	4.6	-	-
132 .	1 minute	6.0	0.6	(very short)
128	5 minutes	9.5	5.4	10
129	10 minutes	9.5	5.8	20
116D	20 minutes	12.4	12.5	55
130	40 minutes	9.8	6.8	95

In the above table, t indicates the time in seconds for 2/3

of R to occur. These results would indicate that a thin film increases the initial strain rate considerably, but an additional increase of the film thickness does not further increase the initial slope, but does significantly increase the time for reversal to occur.

Effect of Etching Time. The experiments performed by Barrett[9, 10] indicate that the reversal should die out if acid-removal of the film is delayed. Investigation along this line failed to verify this finding. Tests were made using E-Cadmium in the standard manner except that the time of replacing water with acid was varied from 200 to 3200 seconds. The resultant plots were shown in Figure 15. The amount of reversal and the time during which the reversal continued increase with increasing time at which acid is added. It is especially noteworthy that when the acid was added at 3200 seconds the run was continued for another six hours at the end of which time the reversal still had not died out! The results of this series are tabulated in Table VII.

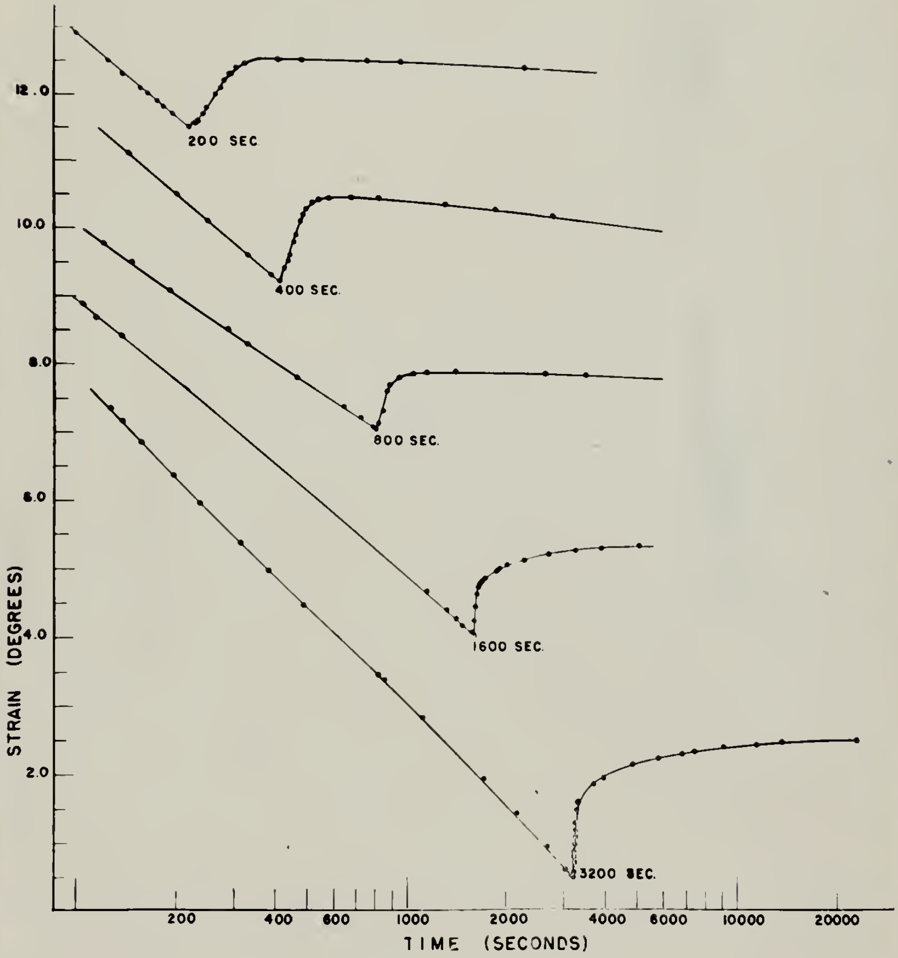


Figure 15. Effect of time of replacing water with acid on after-effect curves. (E-Cadmium)

Table VII

Run No.	Time of adding Acid	S_1	R	R/S_1	t
127	200	11.8	10.0	.85	57
116A	400	12.6)	9.5)		
B	"	13.4)	13.9)		
C	"	12.4) 12.7	11.8) 11.7	.92	60
D	"	12.4)	12.5)		
124	800	10.5	9.5	.91	60
125	1600	12.0	14	1.17	286
126	3200	14.5	20	1.38	550

t, in the above table represents times in seconds for 2/3 of R to occur. Since S_1 varied slightly throughout these runs due to experimental errors it was felt that the ratio of the amount of reversal to the initial slope was more significant than the reversal alone. R, R/S_1 and t all increase with increasing time of adding acid.

Reversal of Film Effect. These investigations led more and more to the belief that surface films directly influence the behavior of the relaxation by their elastic properties rather than by inhibition of dislocations piled up behind the film barriers. Therefore, it seemed desirable to design an experiment in which the effect of the elasticity, if any, of the surface film could be reversed. In order to do this the experiment was conducted with a reversal of the order of anodizing and twisting. In this manner any effect of the surface film should manifest itself by an opposite effect from that so far presented.

Specimens were mounted in the apparatus in the non-anodized condition, and a cylindrical platinum cathode was inserted in the flow tube. The specimen was then twisted 180° in the normal manner and held for 12 minutes. During this time the flow tube was filled with 1N-NaOH and the specimen anodized at 2.5v for 10 minutes. Upon completion of anodization the the flow tube was drained, flushed and filled with distilled water. At the end of the 12 minutes the load was released and the recovery noted. At 400 seconds the water was replaced with acid. The effect was opposite to that previously experienced upon etching. Upon attack with acid, the specimen <u>increased</u> the rate of untwisting rapidly at first and then settled down to a rate which was <u>faster</u> than the original rate. Two of these runs are plotted in Figure 16 as curves -A- and -B-.

As control runs, tests were made on wires treated in the following manner. The specimens were mounted in the apparatus non-anodized as above. They were then anodized for 10 minutes in the apparatus. Following anodization the sodium hydroxide was replaced with water. The specimens were twisted 180°, held for 12 minutes and released. One of these runs is plotted as curve -D- in Figure 16. Its initial slope was greater than the runs described above, and when the acid was admitted the "normal 'abnormal' after-effect" occurred, involving a reversal and settling down to a lesser slope. As

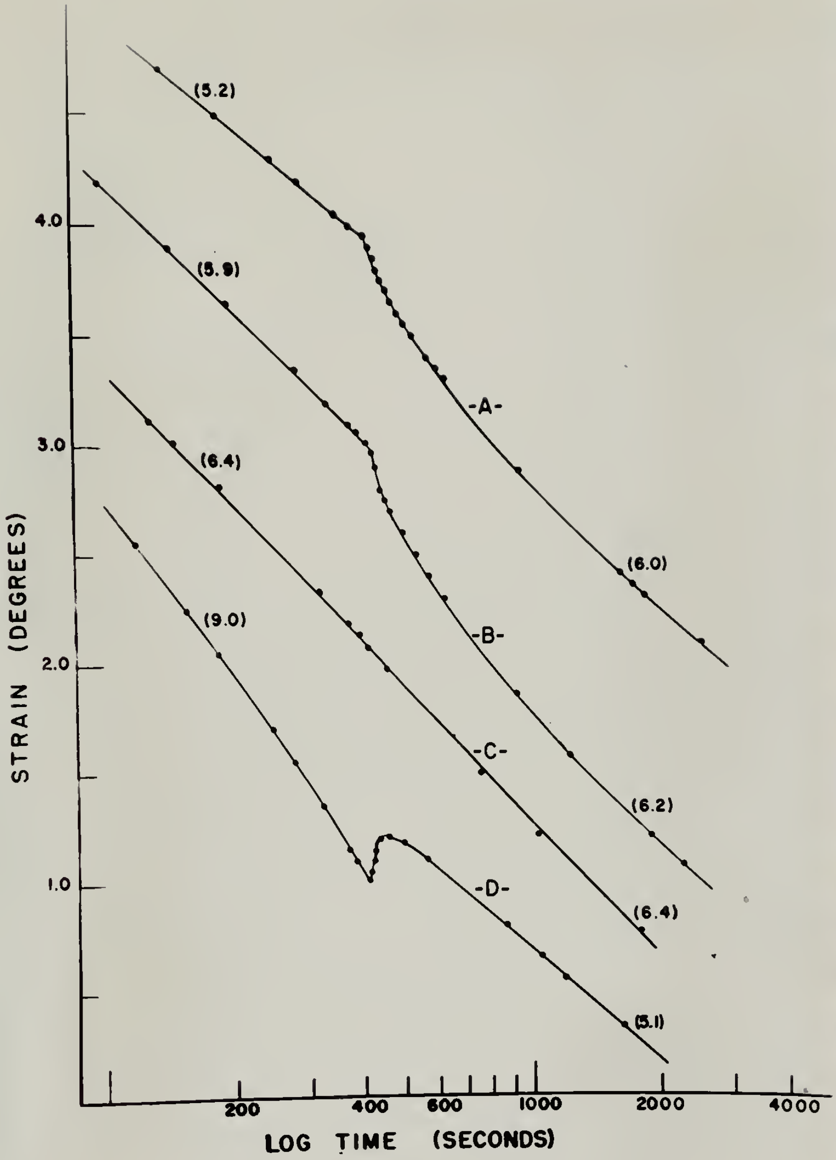


Figure 16. Effect of reversing order of twist and anodization on after-effect curves. Curves -A- and -B- were twisted, anodized, and released; Curve -C- was not anodized, twisted and released; curve -D- was anodized, twisted and released. (E-Cadmium)

a final control, a non-anodized wire was held 12 minutes and then released. Its plot (Curve -C-) shows an intermediate slope. The results of these runs are tabulated below.

Table VIII

Run No.	Anodization	S1	S2	(Figure 16)
134	After twisting	5.2	6.0	-A-
134A	After twisting	5.9	6.2	-B-
136	None	6.4	6.4	-C-
135	Before twisting	9.0	5.1	-D-
135B	Before twisting	8.2	5.1	(not shown)

These runs indicate an influence of the surface film directly, either by its own elastic properties or by the elastic properties that it transmits to the adjacent surface layers of metal. The reproducibility here was fairly good and the trend of relaxation immediately after adding the acid very pronounced, as summarized below.

(1) Anodizing after twist: Low initial strain rate, increasing upon acid attack.

(2) No anodizing: Intermediate strain rate, no effect upon acid attack.

(3) Anodizing before twist: High initial strain rate, decreasing upon acid attack.

Conclusion

The investigation has shown that the effects produced cannot be accounted for by heat effects. During the time that acid was attacking the surface film the acid was circulating past the specimen and dissipating heat. Acid attack on the non-anodized specimens showed no effect on strain rate. No indication of acid attack on the metal was observed either by the formation of gas bubbles on the specimen or by a reduction in specimen diameter measured before and after tests with a micrometer. All tests were made at room temperature and all liquid media were at room temperature during the tests. Control runs were made to indicate the effect of temperature change. These changes, though large, were very short-lived, practically instantaneous and could in no event account for the extremely long lasting effects observed.

The writer concludes, moreover, that the explanation of Barrett[9, 10] cannot be reconciled with the results obtained in this investigation. The pile up and release of dislocations does not account for the marked difference in initial strain rate observed in the specimens with an anodic film and those with clean surfaces. This difference is graphically shown in Figure 11. Further, Barrett's theory assumes that the effect on strain rate would become less when the acid is applied later, assuming that the dislocations piled up beneath the surface layer would migrate back toward the center of the wire

and relieve the stressed condition at the surface. Figure 15 and Table VIII show that the longer the application of acid is delayed the greater is the reversal and the greater is the time during which the reversal lasts. For instance, the reversal still continued after 6 hours when the acid was delayed until 3200 seconds. Finally, the fact that the after-effect caused by acid application is reversed when the order of twisting and anodizing is reversed has not been accounted for by the dislocation pile-up theory.

If the strength and elastic properties of the anodic film itself are considered, a very consistent explanation evolves. The anodic film is considered to be a highly elastic, coherent jacket surrounding the wire specimen. Upon twisting the wire this jacket assumes a highly stressed condition. When the load is released, both the wire and the jacket untwist elastically a very slight amount since most of the deformation of the wire itself was plastic. The wire alone would then, in the absence of a surface film, untwist at its own anelastic rate; however, the anodic film, still in the elastically stressed condition, recovers elastically. The resultant effect is an intermediate untwisting or recovery in which the anelastic rate of the metal is accelerated by the stress residing in the surface film. This accounts for the difference in strain rate of the anodized and non-anodized specimens.

The normal relaxation of a non-anodized wire is time-dependent, and is a function only of ambient temperature and other factors such as physical properties of the metal and dimensions of the specimen. An analogy may be drawn between the wire and the hand of a clock. The clock hand proceeds at its own regulated speed. If the hand were made of rubber, an externally applied torque could accelerate this speed and displace the hand to a more advanced position. When this external force is removed, the hand will return to the position it would have attained without the disturbing influence.

In the case where an anodized wire has been twisted and released, the normal recovery of the wire is forced by the elastic film to proceed at a rate greater than normal. The wire is displaced and assumes a strain and a strain rate different from its normal value. When the film is attacked and dissolved by acid, the wire then assumes the strain and strain rate it would have had under normal conditions. This may be modified if the elastic film has caused the wire to be plastically deformed, so that all of the displacement is not recoverable.

That the wire does not adopt the new strain instantaneously is accounted for by the finite time that is required for the acid to dissolve the film (about 60 seconds by visual observation of a 20-minute, 2.5v film). Figure 14

and Table VI show this. lso, the wire may have been forced to untwist to such an extent by the stress of the film that it now approaches the new strain in a time-dependent fashion; that is, the elastic limit of the wire has been exceeded. This should be especially true when the application of the acid is delayed for a long time. This was demonstrated in Figure 15 for the very long time of reversal in the 3200-second specimen.

Cold work and annealing vary the elastic and plastic characteristics of the metal. The fact that the condition of the metal alters the initial slope and amount of reversal does not exclude the application of the theory. In a larger grained specimen the normal recovery of the metal was not as rapid. With the same thickness of film, the larger grained specimens recovered more slowly, even with the anodic film; and the amount of reversal was correspondingly less.

Finally, the reversal of the order of twisting and anodizing corroborates the theory of film elasticity. When the wire is first twisted and then anodized, the wire is in a stressed condition, whereas the film is in an unstressed condition. Upon release of the load, the normal recovery of the wire is, in this case, retarded by the coherent, elastic film. Removal of the film by acid permits the wire to assume its normal faster strain rate. This effect was shown in Figure 16 and Table VIII. It is natural then that the non-anodized

wire had an intermediate strain rate which was approached by the slopes of the anodized wires after etching.

It is possible to explain the above data on the assumption that it was not the film itself which had the marked elastic properties, but that the presence of the film radically changed the properties of the surface layers of metal. According to Andrade[14] the surface grains of a polycrystalline metal are more easily deformed than those in the interior, since the latter are restrained by grain boundaries on all sides while the former have one free surface. In this case the presence of a surface film could strengthen the surface grains of the wire. However, this effect would be of respectable proportions only in a relatively large grained specimen. In the highly cold worked wires used in these experiments, the grain size was less than 1/100 of the diameter of the wire. Whether a strengthening of the surface grains would have considerable effect with such small grain size is doubtful. On the other hand, remarkable physical properties have often been attributed to very thin films, and in this respect the writer concludes that the findings are similar to the film strength theories discussed by Roscoe,[1] Coffin and Weiman,[8] and Phillips and Thompson[7] in bending and creep experiments.

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Acknowledgements

The writer wishes to express his gratitude to Dr. W. D. Robertson, Associate Professor of Metallurgy, Yale University, for his patient guidance throughout this investigation. Although the findings of this investigation are embarrassingly dissimilar to those of Dr. Barrett, it was he who inspired this work and started the investigations on the right path.

The writer is affiliated with the U. S. Naval Postgraduate School, Monterey, California and his work at Yale University is sponsored by the Office of Naval Research. To both of these institutions he is grateful for making this work possible.

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